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FUNDAMENTAL ASPECTS OF RAPID ClO_2 DELIGNIFICATION OF CONVENTIONAL AND EXTENDED MODIFIED KRAFT PULPS

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ABSTRACT

The bleachability of conventional and extended modified kraft pulps was studied with the bleaching sequence D(EO). These studies demonstrated that high kappa conventional pulps exhibited slightly improved bleaching properties over low kappa pulps. In contrast, the extended modified pulps were found to exhibit equally good bleachability throughout the kappa number range (29-16) studied. Analysis of the residual lignin structure of the bleached pulps suggested that the residual lignin after a D_0 or D(EO) stage was extensively oxidized. Structural analysis studies suggested that the amount of condensed phenolic units present in the residual lignin influenced the bleachability properties.

INTRODUCTION

Recently proposed environmental regulations in North America and continued consumer demand for high-brightness, high-strength pulps has ensured the continued use of chlorine dioxide for bleaching kraft pulps. The need to minimize bleaching costs, improve pulp yields, and enhance the performance of fully bleached pulps have become important research issues. One of the research challenges ahead is to find new ways to improve the delignification and brightening properties of chlorine dioxide.

From a mill perspective, it is well known that the bleachability of kraft pulps can vary substantially. Pulp bleachability can be influenced by a wide array of factors including process variables, such as the efficiency of pulp washing (1) to fundamental chemistry issues, including the structure of residual lignin (2) and carbohydrates in the fiber.(3)

Teder and Sjostrom (4) have demonstrated that alkaline sulfite pulping yields pulps with significantly improved bleachability properties with respect to kraft pulps. Classical studies by Germgard (5) have shown that post-oxygen delignified kraft pulps are less bleachable than pre-O_2 kraft pulps with chlorine dioxide. Recently, studies by Buchert et al. (6, 7) have significantly advanced our knowledge on how carbohydrates, specifically hexenuronic acids, can impact pulp bleachability.

It is also well known that the structure of residual lignin can influence pulp bleachability, especially with chlorine dioxide. This dependency is due, in part, to the reactivity of chlorine dioxide with phenoxy groups. Kumar et al. (8) studied differences in pulp bleachability between

RDH and conventional kraft pulps and suggested a correlation between phenoxy content of the residual lignin and bleachability. Gellerstedt and Al-Dajani (9) have reported that the bleachability of softwood kraft pulps with chlorine dioxide or hydrogen peroxide was influenced by kraft cooking conditions. These differences in bleachability were attributed to differences in residual lignin content, lignin-carbohydrate complexes, and condensed carbohydrates. Froass et al. (10) observed that for softwood kraft pulps, bleachability was influenced by the kappa number of the pulp and the pulping process employed. The total available chlorine (TAC) consumed per unit kappa number reduction in the D(EO) sequence was found to decrease as the kappa number decreased despite the fact that the lower kappa pulps were found to have higher amounts of phenoxy groups. A closer examination of the residual lignin structure prior to bleaching suggested that the amounts of condensed phenolics increased as delignification was extended and it was hypothesized that these units were detrimentally influencing pulp bleachability.

In this paper, we examine the relationship between pulp bleachability and chlorine dioxide delignification for a series of conventional (CK) and pulps from extended modified kraft cooks (EK pulps). The bleachability properties of these pulps were examined after D_0 and D(EO). The D_0 stage was performed using a kappa factor of 0.05 and 0.20 at 10% consistency with high shear mixing and a ClO_2 retention time of 1 min. Previous studies by Schwantes and McDonough (11) have shown that substantial delignification of kraft pulps can be accomplished with reaction times significantly less than what is employed in a typical D_0 stage. The resulting pulps were then alkaline extracted in an oxygen reinforced stage. Pulp bleachability, measured as TAC/Δ(kappa number), was determined after the D_0 and (EO) stage. Residual lignin was isolated before and after each stage and changes in lignin functional groups were determined employing modern NMR methods. This paper summarizes the results of these studies.

EXPERIMENTAL

Materials

All chemicals were commercially purchased and used as received except for p-dioxane, which was purified by distillation over sodium borohydride. All pulps were prepared from a single *Pinus taeda* tree grown in the southeastern part of the USA. The tree was debarked, chipped, and screened. On average, chip thickness varied between 2 - 8 mm.

Kraft Pulping

The kraft pulping experiments were performed at Alhstrom's pilot facilities in Glenns Falls, NY. Established procedures were used to simulate conventional and extended modified continuous (i.e., Lo-Solids®) cooking. (12) Table 1 highlights some of the pulping parameters employed and physical pulp properties.

Table 1. Pulping conditions and pulp properties from CK and EK pulps.

	Conventional Kraft Pulps (CK)			Extended Modified (EK) Continuous Kraft Pulps		
Kappa #	33.0	21.3	14.7	29.3	19.1	16.0
Viscosity mPa	32.6	22.6	13.3	43.4	25.5	19.2
Max. Temp °C	168	170	171	160	166	170
H-Factor	1201	1999	3496	2003	3362	4489
Total EA Consumed %on wood	14.8	15.4	16.7	14.1	15.0	16.6

Rapid Do

Employing the quantum reactor, a 3% consistency pulp mixture was heated to 45°C and the pH was adjusted to either 5.0 or 4.0 for kappa factor 0.20 and 0.05 ClO_2 bleaching experiments, respectively. ClO_2 (kappa factor of either 0.05 or 0.20) was added into the quantum reactor and the pulp was mixed for 30 sec at 15 Hz and the mixer was then stopped for 30 sec, after which a quenching solution of aqueous Na_2SO_3 (mass Na_2SO_3 added=mass applied ClO_2 x 4.67) was injected. The pulp mixture was then stirred for an additional 30 sec., filtered, and characterized. Kappa number was then determined.

(EO)-Stage

The pulp from the Do stage was thickened to 25% consistency, without washing, thoroughly disintegrated and added to a pin mixer. The consistency was adjusted to 10% and the pulp was then extracted under typical (EO) conditions: NaOH charge was chosen to yield a terminal pH of 10.7-11.5. The (EO) stage was performed at 70°C for 60 min. The initial O_2 pressure was 60 psig and this was decreased 10 psig every 5 min. At the end of the (EO) stage, the pulp consistency was adjusted to 3%, the effluents were collected, and the pulp was thoroughly washed.

Residual Lignin Isolation

Isolation of residual lignin from the softwood kraft pulps was accomplished employing standard literature methods (13, 14, 15). In brief, air-dried pulp (40 gr oven-dry weight) was added to an aqueous 1.00 N HCl (100 ml), p-dioxane (900 ml) solution and this mixture was then refluxed for 2 hr under an argon atmosphere. The mixture was then filtered, concentrated, and purified by precipitation. This procedure afforded, on average, 30-55% yield of residual lignin as summarized in Table 2.

^{1}H NMR Analysis of Residual Lignin

The lignin samples were dissolved in anhydrous DMSO-d_6. Sodium-3-trimethylsilyl propinate-2,2,3,3-D_4 was added as an internal standard and the samples were analyzed using a 400 MHz Bruker DMX NMR spectrometer. The analyses were accomplished employing a $\pi/2$ pulse, 25-sec delay, 12,000 Hz sweep width, and 240 transients. The FID was fourier transformed with 1 Hz of line broadening and one degree of zero filling. Data analysis was accomplished using the method recently reported by Li and Lundquist.(16)

Table 2. Yield of lignin recovered from brownstock and bleached pulps.

CK Pulp	%Lignin Yield[a]	EK Pulp	%Lignin Yield
CK32.4:pulp	58	EK29.3:pulp	52
D_0	35	D_0	30
(EO)	36	(EO)	36
CK21.3:pulp	54	EK19.1:pulp	48
D_0	29	D_0	30
(EO)	29	(EO)	28
CK14.7:pulp	57	EK15.6:pulp	55
D_0	30	D_0	28
(EO)	39	(EO)	29

[a]% lignin recovered=(mass of lignin recovered)/(kappa number of pulp x oven dry weight of pulp x 0.15%)

^{31}P NMR Spectroscopy

Lignin samples were phosphorylated with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane following the procedure of Argyropopoulos (17) and analyzed by ^{31}P-NMR.

RESULTS AND DISCUSSION

Bleachability of Kraft Pulps

Recent studies at IPST have shown that the rapid kinetics of chlorine dioxide delignification of kraft pulps can be utilized for bleaching provided that good uniform mixing can be accomplished. Preliminary studies reported by Schwantes, demonstrated that most of the delignification of a D_0-stage is accomplished within the first 1-2 minutes of bleaching, provided that the bleaching chemical is uniformly distributed throughout the bleaching reactor.(7) This type of very short bleaching stage, referred to as Rapid D_0, reduces AOX formation and offers significant savings in bleach plant capital equipment. This paper examines the results of applying this process in the delignification of a series of softwood kraft pulps manufactured under conventional and conditions and conditions that correspond to Lo-Solids® cooking, a modified kraft pulping process designed to allow delignification to be extended to low kappa numbers without loss of pulp quality. This was of interest because the short retention time is expected to yield bleached pulps having lignins whose structural features are unaffected by secondary reactions. In what follows, the Lo-Solids® pulps are referred to as extended (EK) pulps. The results of the bleaching studies are summarized in Table 3.

The results summarized in Table 3 indicate that the conventional pulps exhibited only slightly improved bleachability at higher lignin contents when the ClO_2 retention time is kept short. The EK pulps were equally bleachable at high and low lignin contents under these conditions. These results differ somewhat from those of earlier studies by our group (18) indicating that the decreased bleachability of low-kappa pulps at normal D_0 retention times is related to inhibition of reactions that occur after the initial phase.

Table 3. Bleachability of CK and EK pulps towards Rapid D_0 and EO.

Pulp	k.f.	TAC	Δ Kappa	TAC/Δ Kappa
CK-32.4	0.05	1.62	D - 5.9 EO-13.6	0.274 0.119
CK-32.4	0.20	6.48	D - 15.3 EO-24.3	0.423 0.267
CK-21.3	0.20	4.26	D - 9.2 EO-15.3	0.463 0.278
CK-14.7	0.20	2.94	D - 6.5 EO-10.6	0.452 0.277
LS-29.3	0.05	1.46	D - 5.1 EO-13.0	0.286 0.112
LS-29.3	0.20	5.86	D - 13.7 EO-22.2	0.428 0.264
LS-19.1	0.20	3.82	D - 8.8 EO-14.6	0.434 0.262
LS-15.6	0.20	3.12	D - 6.9 EO-11.8	0.452 0.264

The EK pulps were modestly easier to delignify than the conventional pulps, requiring a ClO_2 charge that was an average of 4% lower than in the case of CK for a given kappa number reduction measured after the (EO) stage. The TAC/$\Delta\kappa$ values were larger than normally observed at normal retention times in the D_0 stage because no credit was taken for the unutilized residual remaining after only one minute. In order to limit the D_0 reaction time to exactly one minute, it was necessary to stop the reaction by injection of sulfite, which destroyed the residual and precluded its measurement. It is for this reason that, in practical applications, low kappa factors are recommended for Rapid D_0.

Residual Lignin Analysis

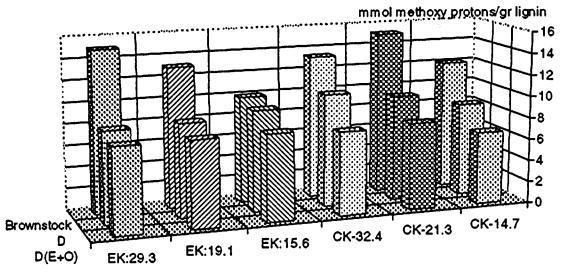
The difference in bleachability between the CK and EK pulps suggests that it may be possible to tailor pulp properties to a bleaching chemical. However, before such a strategy can be rationally designed, the fundamental principles involved in bleachability must be determined. Over the last 10 years, our knowledge of residual lignin structure in kraft pulps has grown tremendously. Early studies by Gierer (19), Gellerstedt (20,21,22) and Dimmel (23) documented the changes in lignin structure during a kraft cook. These studies established that as cooking proceeds, numerous changes occur in residual lignin, including an increase in residual lignin phenoxy content and a decrease in β-O-aryl ether content.

Having established these important pulping reactions, several researchers have now focused on elucidating how process changes in the kraft pulping can moderate the structure of residual lignin. Studies by Hortling et al.(24) have compared the differences in residual lignin that occur between Superbatch and conventional kraft pulps. Gellerstedt (9) has reported differences in bleachability of Scandinavian softwood kraft pulps dependent upon how they are cooked. Jiang and Argyropoulos (25) have found that residual lignin from modified continuous kraft pulping procedures has lower amounts of condensed phenolic units and higher amounts of carboxylic acids as compared to lignin isolated from conventional kraft pulps. Froass et al. have shown that pulps prepared under simulated conventional and EMCC® conditions exhibited differences in residual lignin structure and bleachability (10). It was hypothesized in these latter studies that condensed phenoxy groups and β-O-aryl ether groups may influence chlorine dioxide bleachability of kraft pulps.

This study seeks to further examine the relationship between pulp bleachability and residual lignin structure. The pulps examined in this study were all prepared from a common wood source. This facilitated comparisons of residual lignin structures before and after bleaching with D(EO).

In an earlier report, we examined the structure of the residual lignin present in the kraft pulps employed in this bleaching study. The results of these studies suggested the CK and EK pulps had comparable lignin functional groups at kappa numbers of approximately 30. As delignification was extended, the CK pulps were found to have higher amounts of phenolics and methoxy groups than the EK pulps. To further explore the relationship between bleachability and residual lignin structure, we isolated residual lignin structure after the Rapid D_0 and (EO) stages employed in the current study. The residual lignin samples isolated from these pulps were analyzed by ^1H NMR according to the method of Li and Lundquist.(16) This procedure provides a convenient method of determining the concentration of phenolic units, carboxylic acids, and methoxy groups in residual lignin. The changes in methoxyl content for the unbleached and bleached pulps is summarized in Figure 1.

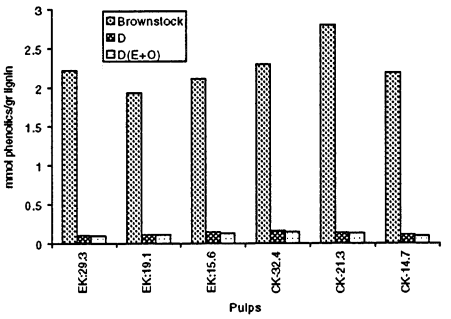
Figure 1. Methoxyl proton content for residual lignin from brownstock, D, and D(EO) CK and EK pulps as determined by ^{1}HNMR.



The decrease in methoxy content from the brownstock to the Rapid D_0 bleached pulps is a result of the demethoxylation chemistry associated with chlorine species in the D_0 stage. The additional decrease in methoxy content measured after the (EO) stage can be attributed, in part, to the hydrolysis of muconic acid methyl esters during alkaline extraction. Nonetheless, the largest loss in methoxy content occurred during the Rapid D_0 stage.

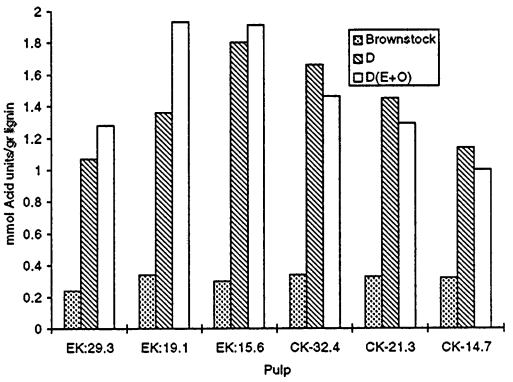
Another group of significant interest in chlorine dioxide bleaching is the phenolic unit. The use of proton NMR provides a method of monitoring the changes in the concentration of this functional group as pulping and bleaching proceeds. The results of this analysis for the LS and CK pulps are summarized in Figure 2.

Figure 2. Phenoxy proton content for residual lignin from brownstock, D, and D(EO) CK and EK pulps as determined by ^{1}H NMR.



The results of this analysis suggested that the Rapid D_0 stage was efficient at removing most of the phenolics from the residual lignin isolated for these studies.

Figure 3. Carboxylic acid proton content for residual lignin from brownstock, D, and D(EO) CK and EK pulps as determined by ^{1}H NMR.

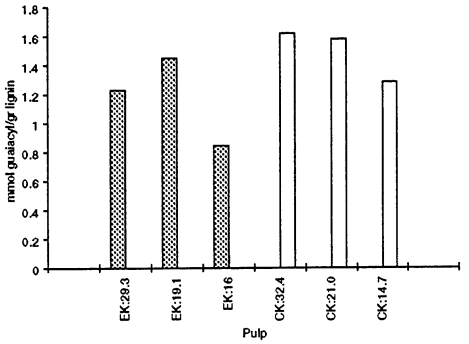


As expected, the extensive oxidation of lignin yielded a residual lignin that contained a significant enrichment of acid groups, as summarized in Figure 3.

In light of these substantial structural changes in the residual lignin, the parameters contributing to differences in bleachability become more difficult to elucidate. Nonetheless, a close inspection of the residual lignin components of the starting pulps did suggest a possible contributing factor. The CK pulps studied in this report have both higher noncondensed and condensed phenoxy structures. Perhaps

most notable is the increased amounts of condensed phenolics, as shown in Figure 4.

Figure 4. Condensed guaiacyl proton content for residual lignin for CK and EK pulps as determined by ^{31}P NMR.



The results of the ^{31}P NMR analysis of the phosphitylated residual lignin samples suggests that the conventional pulps have higher amounts of condensed lignin than the EK pulps. Hence, the CK pulps, despite having higher total phenolic concentration, are less reactive to chlorine dioxide due possibly to the increased amounts of condensed phenolics. [Note: Lignin phosphitylation/ ^{31}P NMR analysis was employed so as to facilitate comparisons with our previous studies].

It is interesting to compare the results of this analysis with our prior studies on conventional and EMCC® pulps. The results of pulp bleachability studies for these latter pulps and the phenolic content of the residual lignins is summarized in Table 4.

Table 4. Kraft residual lignin structure and bleachability of EMCC® and conventional softwood kraft pulps bleached via $D_0(E+O)$.

Pulp[1]	TAC[2]/Δ Kappa	mmol total phenolics/gr lignin[3]	mmol condensed phenolics/gr lignin
E:29	0.21	2.07	0.91
E:18	0.22	2.15	0.94
C:28	0.21	2.07	0.89
C:18	0.23	2.29	0.99

[1]E pulps were prepared via simulated EMCC® conditions, C pulps were prepared under simulated conventional kraft conditions, kappa number of the unbleached softwood kraft pulp is given after the letter; [2]pulps were bleached under conventional D_0 (0.20 k.f.) (E+O)-stages, see Froass et al. for experimental further details; [3]lignin isolated in the same manner as employed in this paper.

Our results with the CK pulps mirror the results summarized in Table 5. As the kappa number of the CK or C pulp was lowered from the 30's to the mid-20's the phenoxy content increases and bleachability decreases. In each case, this can be attributed to the increase in condensed phenolic lignin units. The EK pulps do not have the same profile of condensed lignin and presumably this explains the differences in bleachability between the EK pulps and the E pulps in Table 4.

CONCLUSIONS

Modifying the kraft pulping process offers promise as a means of controlling the bleachability of kraft pulps. By modifying the pulping process, it is possible to alter the nature of residual lignin and this can impact chlorine dioxide delignification chemistry. The results of these studies suggest that condensed phenolics contribute to the overall bleachability of kraft pulps. Before a complete description of pulp bleachability can be provided other factors including the

role of lignin-carbohydrate complexes need to be investigated.

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